# Bazzanene, a Sesquiterpene Hydrocarbon of a New Carbon Skeleton from *Bazzania pompeana* (Lac.) Mitt.

A sesquiterpene hydrocarbon of a new carbon skeleton was isolated from the essential oil of *Bazzania pompeana* (Lac.) Mitt., and its structure was determined as formula (I). We propose the name bazzanene for this hydrocarbon, and the evidences for the proposed structure are described here.

Bazzanene was isolated in a pure state with respect to gas and thin-layer chromatography by means of fractional distillation and successive elution chromatography using silica gel impregnated with silver nitrate. This compound, $C_{15}H_{24}$, showed the following physical properties: bp 102–103°/2 Torr; $[\alpha]_D^{25} + 48.0°$; $\nu_{max}^{liq}$ 1647, 886 cm$^{-1}$ (–C=CH$_2$), 806 cm$^{-1}$ (–C=CH) and 1379, 1369 cm$^{-1}$ (CMe$_2$); $\delta_{ppm}^{CDCl_3}$ 0.83 (3H, s, –C–CH$_3$), 1.02 (3H, s, –C–CH$_3$), 1.64 (3H, d, $J$ = 1.2 Hz, –C=CH$_3$), 4.83, 4.96 (each 1H, s, –C=CH$_2$) and 5.32 (1H, m, –C=CH); M$^+$ peak m/e 204 (5%), base peak m/e 109, next highest peak m/e 67 (31%) and third highest peak m/e 93 (25%).

This hydrocarbon took up 2 moles of hydrogen in catalytic hydrogenation over the Adams catalyst in acetic acid to produce a saturated tetrahydro compound, $C_{15}H_{28}$ (M$^+$ peak m/e 208 and base peak m/e 96), and heating with palladium-charcoal in a sealed tube it produced cuparene (II) in a good yield, which was identified by IR-, NMR- and mass-spectrometry.

Bazzanene is thus deduced to be a bicyclic sesquiterpene hydrocarbon which bears one geminal dimethyl, one methyl on a double bond and one exo-methylene and gives cuparene on dehydrogenation. As such structures, only 3 carbon skeletons (III), (IV) and (V) are probable. Among these skeletons, (IV) is himachalane[1] and (V) is chamigrane[2], and IR- and mass-spectra of both these compounds did not coincide with those of the saturated

compound of bazzanene. Therefore, bazzanene can be considered to have a carbon skeleton of (III), which is also supported by the following fact: both himachalane and chamigrane exhibited a base peak at m/e 124, whereas the tetrahydro product of bazzanene exhibited it at m/e 96 together with a characteristic peak at m/e 111 (51%), to which the fragment ions (VI) and (VII) expected from structure (III) can be assigned.

Bazzanene was oxidized with sodium dichromate in acetic acid to produce an $\alpha,\beta$-unsaturated ketone, $C_{15}H_{22}O$ (calcd. m/e 218.167, obsd. m/e 218.166), $\nu_{max}^{liq}$ 1672 cm$^{-1}$, $\lambda_{max}^{EtOH}$ 239 nm ($\varepsilon$ 8300; calcd. 239 nm for CH$_3$–C=CH–CO–). The NMR-spectrum, $\delta_{max}^{CDCl_3}$ 0.99 (3H, s, –C–CH$_3$), 1.09 (3H, s, –C–CH$_3$), 1.74 (3H, d, $J$ = 1.5 H$_2$, –C=C–CH$_3$), 2.33 (2H, d, $J$ = 1.0 Hz, –CH$_2$–CO–), 4.83, 5.02 (each 1H, s, –C=CH$_2$) and 6.50 (1H, m, –C=CH–CO–), and the characteristic peaks of the mass spectrum, m/e 95 (100%, $C_7H_{11}$: calcd. m/e 95.086, obsd. m/e 95.086) (IX) and m/e 123 (77%, $C_8H_{11}O$: calcd. m/e 123.081, obsd. m/e 123.082) (X), can be explained by structure (VIII) expected for the oxidized product of structure (I).

Therefore, bazzanene must be 2,6,6-trimethyl-8-methylene bicyclo[5.3.1]undec-2-ene. This is the first example of a bicyclo[5.3.1]undecane system in sesquiterpene compounds.

*Zusammenfassung.* Aus dem essentiellen Öl von *Bazzania pompeana* (Lac.) Mitt. wurde Bazzanen, ein Sesquiterpen-Kohlenwasserstoff mit einem neuartigen Kohlenstoffgerüst, isoliert. Bazzanen besitzt die Struktur des 2,6,6-Trimethyl-8-methylen bicyclo[5.3.1.]undec-2-ens.

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(I)          (II)



(III)          (IV)          (V)
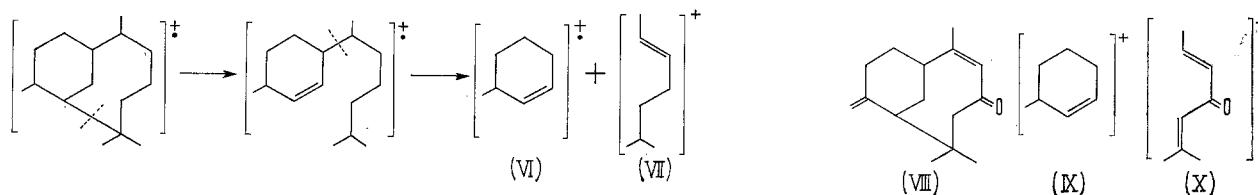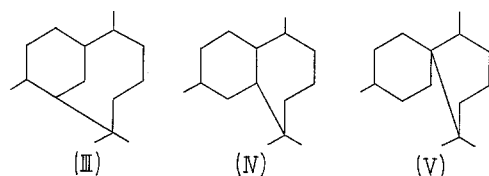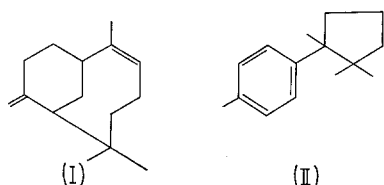
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(VI)          (VII)          (VIII)          (IX)          (X)